

# C<sub>3</sub>—M<sub>α</sub> Bond Contribution to Polarizability Tensor and <sup>3</sup>J(C<sub>1</sub>M<sub>α</sub>) NMR Coupling Constant in 1-X-3-M-Bicyclo[1.1.1]Pentanes

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**ABSTRACT:** In the present work, the relationship between the large substituent effects on <sup>3</sup>J(C<sub>1</sub>H) in 1-X-3-M-bicyclo[1.1.1]pentanes, **I**, and the polarizability of the bridgehead C<sub>3</sub>—M<sub>α</sub> bond is investigated. The existence of such a relationship is suggested by the finding that the effect of an electronegative substituent X on <sup>3</sup>J(C<sub>1</sub>M<sub>α</sub>) couplings in **I** (M = H) is due to a distortion of the C<sub>3</sub>—H bond toward the C<sub>1</sub> center, which enhances the Fermi contact interaction. If such distortion originates in an electrostatic effect, then in other members of this series it can be expected that the substituent effects on <sup>3</sup>J(C<sub>1</sub>M<sub>α</sub>) couplings should depend strongly on the C<sub>3</sub>—M<sub>α</sub> bond polarizability. Two approaches are followed. First, the *ab initio* CLOPPA-IPPP method is applied to study the C<sub>3</sub>—M<sub>α</sub> bond contribution to the molecular static polarizability tensor in **I** (M = H, F, CH<sub>3</sub>). Such bond polarizabilities are found to follow the same trend as calculated as well as experimentally determined substituent effects on <sup>3</sup>J(C<sub>1</sub>M<sub>α</sub>) couplings, which were measured as part of this work in **I** [X = H, Cl; M = F, CH<sub>3</sub> and X = OCH<sub>3</sub>; M = Sn(CH<sub>3</sub>)<sub>3</sub>]. Second, <sup>3</sup>J(C<sub>1</sub>M<sub>α</sub>) couplings

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( $M = \text{H}, \text{CH}_3$ ) are calculated at an *ab initio* level for  $X = \text{H}, \text{F}$ , and they are compared with those obtained in the parent compound ( $X = \text{H}$ ) if the calculation is carried out in the presence of an inhomogeneous electric field. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 181–188, 1998

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## Introduction

Substituent effects on NMR spin–spin coupling constants in a family of compounds are usually small compared with the corresponding coupling in the reference compound. If the substituent effect on a given coupling constant is defined by the ratio between that coupling in the substituted compound and the corresponding one in the parent compound,  $E_{(X)} = J_{\text{NM}}^{(X)} / J_{\text{NM}}$ , then  $E_{(X)}$  is a number close to one.

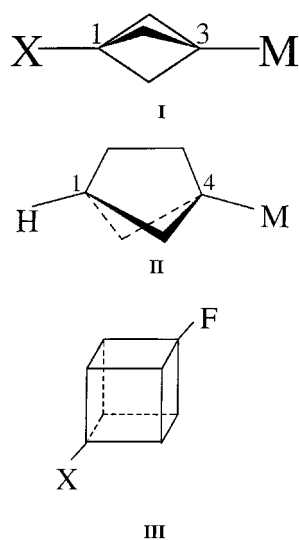
A conspicuous exception to this rule was determined in a previous study<sup>1</sup> for 1-*X*-bicyclo[1.1.1]pentanes, **I** ( $M = \text{H}$ ), Scheme 1, where, for  $^3J(\text{C}_1\text{H})$  couplings surprisingly large values of  $E_{(X)}$  were measured for some substituents. For instance, for  $X = \text{Br}$  a value of  $E_{(X)}$  as large as 3.8 was obtained. Such extremely large substituent effects were found: (a) to correlate rather well with the substituent electronegativity; and (b) that theoretical bond contribution analyses

of such effects carried out with the CLOPPA-IPPP method<sup>2,3</sup> (Contributions from Localized Orbitals within the Polarization Propagator Approach–Inner Projections of the Polarization Propagator) yielded, as the main factor defining such  $E_{(X)}$  values, an enlargement of the rear lobe of the LMO corresponding to the bridgehead  $\text{C}_3\text{—H}$  bond, owing to the electronegativity of the *X* substituent. The increase in size of that rear lobe, yielded an increase in the electronic density associated with that bond at the site of  $\text{C}_1$  which, in turn, rendered an increase in the Fermi contact interaction that defines that  $^3J(\text{C}_1\text{H})$  coupling constant.

Point (a) suggests the following rationalization: Owing to the electronegativity of the *X* group, the  $\text{X—C}_1$  bond is polarized as  $\text{X}(-)\text{—C}_1(+)$ , which creates an electric field along the  $\text{C}_3\text{—H}$  bond. This electric field renders a displacement of the electronic density associated with this bond, yielding the effect described in (b).

Should this be a sound rationalization, then the  $E_{(X)}$  substituent effect for coupling constants of type  $^3J(\text{C}_1M_\alpha)$  in families with different *M* substituents in **I**, would depend on the polarizability of the  $\text{C}_3\text{—}M_\alpha$  bond, that is,  $E_{(X)}$  would depend on the response of this bond to the electric field quoted above.

In the present study, such a conclusion is analyzed from theoretical and experimental points of view. Theoretically, two approaches are used. On the one hand, bond contributions to the molecular static polarizability tensor are compared for different  $\text{C}_3\text{—}M_\alpha$  bonds in **I** ( $M = \text{H}, \text{F}, \text{CH}_3$ ). These are calculated with the CLOPPA-IPPP method recently extended to include this response property.<sup>4</sup> On the other hand, the  $^3J(\text{C}_1M_\alpha)$  couplings in **I** ( $X = \text{H}, \text{F}$ ;  $M = \text{H}, \text{CH}_3$ ), are calculated at the *ab initio* level, and then they are compared with those obtained in the same compound if the calculation is performed in presence of an inhomogeneous electric field which intends to mimic that produced by the  $\text{X}(-)\text{—C}_1(+)$  polar bond. Experimentally,  $^3J(\text{C}_1M_\alpha)$  coupling constants are mea-



SCHEME 1.

sured in **I** for  $X = \text{H, Cl, or OCH}_3$ ; and  $M = \text{F, CH}_3$ , and  $\text{Sn}(\text{CH}_3)_3$ .

## Methods

The CLOPPA-IPPP method for calculating local polarizabilities was implemented in the System Modena (SYSMO) program,<sup>5–7</sup> which is based on the equation of motion method<sup>8</sup> for computing the polarization propagator (PP) at the RPA level. Indirect nuclear spin–spin coupling constants were also calculated with the SYSMO program. Molecular geometries were optimized with the GAMESS program.<sup>9</sup> In all cases, calculations were carried out using the 6-31G\*\* basis set.<sup>10</sup>

## LOCAL POLARIZABILITIES AND OCCUPIED LMO POLARIZABILITIES

As the CLOPPA-IPPP method for analyzing molecular polarizabilities is described elsewhere,<sup>4</sup> only a brief overview of its main features is given here. This approach is intended for decomposing molecular polarizabilities into “local” contributions starting from a unideterminantal ground-state wave function. Within this approach, the “local polarizability,” that is, the polarizability of a molecular fragment, is calculated within the PP approach at the RPA (random phase approximation) level, by means of the inner-projections technique<sup>11</sup> applied onto the molecular fragment of interest. The electronic structure of the molecular fragment is represented in terms of orthogonal localized molecular orbitals (LMOs) which closely resemble the chemical notions of bonds, lone pairs, cores, and antibonding orbitals. Occupied and vacant LMOs are obtained by means of unitary transformations applied separately to canonical occupied and vacant molecular orbitals (MOs). Vacant LMOs can be localized on one or several centers. Those vacant LMOs localized on two centers involved in a chemical bond can be ascribed to antibonding LMOs. The localization procedure used in this work is Engelmann’s,<sup>2,12</sup> which is a generalization of Verwoerd’s,<sup>13</sup> used in a repetitive fashion.

The polarizability tensor can be written within the PP approach as<sup>14</sup>:

$$\tilde{\alpha} = 2(\tilde{r}|Q)^1 P(Q|\tilde{r}) \quad (1)$$

where  ${}^1P$  is the singlet part of the PP matrix:  $Q^+ = a^+i$  are excitation operators of one particle,

where  $i$  stands for an occupied HF spin orbital and  $a$  for a vacant one; and  $(\tilde{r}|Q) = \langle 0|[\tilde{r}^+, Q]|0\rangle$  is written in superoperator formalism.<sup>14</sup>

The “local” contribution to the  $rs$ -Cartesian component of the polarizability tensor ( $r, s = x, y, z$ ); that is, the contribution due to a molecular fragment,  $\alpha^{L,rs}$ , is defined by rewriting eq. (1) in the LMO basis:

$$\begin{aligned} \alpha^{L,rs} &= -2 \sum_{ia \leq jb}^{\text{local}} (\langle a|x_r|i\rangle W_{ia,jb} \langle b|x_s|j\rangle \\ &\quad + \langle b|x_r|j\rangle W_{ia,jb} \langle a|x_s|i\rangle) \\ &= \sum_{ia \leq jb}^{\text{local}} \alpha_{ia,jb}^{L,rs} \quad (r, s = x, y, z) \quad (2) \end{aligned}$$

where  $i$  and  $j$  are occupied LMOs and  $a$  and  $b$  are vacant LMOs. The sum in eq. (2) is restricted to the subset of LMOs that define the chosen molecular fragment.  $W_{ia,jb}$  is the element of the singlet PP matrix block which corresponds to a real perturbation, inner-projected onto the subset of LMOs that define the chosen fragment.

Each term of the sum in eq. (2),  $\alpha_{ia,jb}^{L,rs}$ , involves at most two occupied and two vacant LMOs and indicates to what extent the  $a$ -vacant LMO contributes to the polarization induced in the  $i$ -occupied LMO by the effect of intramolecular interactions, as the  $j$ -occupied LMO is coupled with the  $b$ -vacant LMO by the external perturbation; that is, the electric field. However, it must be noted that  $W_{ia,jb}$  depends on all LMOs belonging to the local fragment and, thus, each  $\alpha_{ia,jb}^{L,rs}$  contains the influence of the whole fragment under consideration.

Contributions to the polarizability tensor, which depend only on occupied LMOs, can be defined by summing in eq. (2) over the vacant ones belonging to the local fragment:

$$\alpha_{ij}^{L,rs} = \sum_{a,b}^{\text{local}} \alpha_{ia,jb}^{L,rs} \quad (3)$$

These terms can be interpreted as follows.<sup>4</sup> An external electric field,  $\vec{E} = E_r \hat{x}_r$ , considered as a perturbation connects the occupied LMO  $|j\rangle$  with the vacant LMOs. Owing to such a perturbation, another occupied LMO  $|i\rangle$  is modified and the  $s$ -component of its dipole moment results:

$$\langle \tilde{i}_j | x_s | \tilde{i}_j \rangle = \langle i | x_s | i \rangle + 2E_r \sum_{ab} \langle i | x_s | a \rangle^1 P_{ia,jb} \langle b | x_r | j \rangle \quad (4)$$

where  $|\tilde{i}_j\rangle$  is the corrected  $|i\rangle$  LMO up to the first order owing to the perturbation on  $|j\rangle$ . From eq. (4), it follows that:

$$\alpha_{ij}^{L,rs} = \frac{1}{E_r} \left[ \langle \tilde{i}_j | x_s | \tilde{i}_j \rangle - \langle i | x_s | i \rangle \right] \tag{5}$$

Thus, the  $\alpha_{ij}^{L,rs}$  terms can be interpreted as the *s*-component of the induced dipole moment on the  $|i\rangle$ -occupied LMO (per unit field) due to the polarization of the  $|j\rangle$  LMO in the presence of the external field,  $\vec{E}$ . These types of terms are considered “mutual” polarizabilities.<sup>4</sup>

In the same way, if the perturbation connects the  $|i\rangle$ -occupied LMO with the vacant LMOs of the local subspace:

$$\alpha_{ii'}^{L,rs} = \frac{1}{E_r} \left[ \langle \tilde{i} | x_s | \tilde{i}' \rangle - \langle i | x_s | i \rangle \right] \tag{6}$$

is obtained, which is the dipole moment (per unit field) of the LMO  $|i\rangle$  induced by the external field; that is, the polarizability of the occupied LMO  $|i\rangle$  on the fragment considered. If the  $|i\rangle$ -occupied LMO represents a bond,  $\alpha_{ii'}^{L,rs}$  is referred to as the “bond” polarizability of the *i* bond. It is noteworthy that the  $\alpha_{ii'}^{L,rs}$  terms depend on the subset of vacant LMOs, which are included in the chosen fragment, and thus it yields an idea on how vacant LMOs of different molecular regions contribute to the polarization of the  $|i\rangle$ -occupied LMO, because the external electric field connects  $|i\rangle$  with those vacant LMOs.

Results and Discussion

The component of the  $C_3-M_\alpha$  bond polarizability tensors along the  $C_3-M_\alpha$  direction in **I** ( $X = H$ ;  $M = H, F$ , and  $CH_3$ ) are displayed in the first row of Table I. These bond polarizabilities are defined using the following subspace of occupied and vacant LMOs: occupied LMO—that of the  $C_3-M_\alpha$  bond; vacant LMOs—all those localized in the  $C_3$  and  $M_\alpha$  atoms. In this way, only the local effect on this bond is taken into account. A conspicuous difference for the  $C_3-H$ ,  $C_3-F$ , and  $C_3-C$  bond polarizabilities is observed, the largest being that of the  $C_3-H$  bond. This trend is thought to originate mainly in the different excitation energies of these three compounds in the considered subspace; that is, it should be easier to obtain excitations within the  $C-H$  electronic sys-

TABLE I.  
Bond Polarizabilities of Bridgehead  $C_3-M_\alpha$  Bond ( $M = H, F, CH_3$ ),  $\alpha_{C-M}$  and  $\alpha'_{C-M}$ , and of  $C-H$  Bond,  $\alpha_{C-H}$ , in **I** ( $X = H$  and  $M = H, F, CH_3$ ) (All Values in a.u.).

	<i>M</i> = H	<i>M</i> = F	<i>M</i> = C
(a) 1- <i>X</i> -bicyclo[1.1.1]pentane			
$\alpha_{C-M}^a$	1.66	1.38	0.94
$\alpha'_{C-M}^b$	1.70	1.40	0.99
$\alpha_{C-H}^c$	1.66	1.65	1.67
(b) $CH_3M$			
$\alpha_{C-M}^a$	2.70	1.62	1.09

<sup>a</sup>Calculated considering  $C-M$ -occupied and vacant LMOs as local subspace.  
<sup>b</sup>Calculated considering  $C-M$ -occupied and vacant  $C-H$  vacant LMOs as local subspace.  
<sup>c</sup>Calculated considering  $C-H$ -occupied and vacant LMOs as local subspace.

tem than in the  $C-F$  or  $C-C$  ones. It is of interest to note that the respective optimized bond lengths follow the opposite trend than that of the bond polarizability; that is, the largest bond polarizability corresponds to the shortest bond length. As found previously<sup>1</sup> the substituent effect,  $E_{(X)}$ , on  $^3J(C_1H)$  coupling constants in **I** ( $M = H$ ) is mainly originated in distortions of the  $C_3-H$  bond electronic distribution owing to the electronegativity of the *X* substituent. For other *M* groups, this distortion should follow the  $C_3-M_\alpha$  bond polarizabilities. Therefore, it can be expected that, in these compounds, the  $E_{(X)}$  [i.e., the substituent effects on  $^3J(C_1H)$ ,  $^3J(C_1F)$ , and  $^3J(C_1C_{Me})$  coupling constants] should follow a similar trend. However, a direct proportionality between  $E_{(X)}$  and the  $C_3-M_\alpha$  bond polarizability should not be expected because other factors are also affecting these coupling constants.

To assess to what extent the  $C_3-M_\alpha$  bond polarizability is influenced by excitations involving the vacant LMOs localized on the  $C_1-X_\alpha$  bond, values obtained when considering all excitations from the  $C_3-M_\alpha$ -occupied LMO to all the vacant LMOs localized either on the  $C_3-M_\alpha$  or the  $C_1-X$  bond are displayed in the second row of Table I. It is observed that only minor corrections to values shown in the first row are obtained. Thus, it is concluded that the main features of bond polarizabilities are adequately taken into account when considering only the subset of vacant LMOs considered in the first row.

In compounds **I** with  $X = \text{H}$  and  $M = \text{H, F, and CH}_3$ , the C<sub>1</sub>—H bond polarizabilities were also calculated to determine if they depend on the substitution at the other bridgehead carbon atom. The corresponding values are displayed in the third row of Table I and, when compared with that of the first row, only minor variations are observed.

It is known<sup>15</sup> that the strain of the cage substrate in compounds of type **I** is very important. To assess how such strain affects bond polarizabilities shown in the first row of Table I, C—M<sub>α</sub> bond polarizabilities calculated in CH<sub>3</sub>M ( $M = \text{H, F, CH}_3$ ) compounds are displayed. A notably lower value of bond polarizability is observed in the strained compounds than in the unstrained ones, especially for the C—H bond. This large difference can be rationalized in terms of the different hybridization at the C atom. In fact, the conspicuously larger value of the bridgehead <sup>1</sup>J(CH) coupling constant in bicyclo[1.1.1]pentane, than <sup>1</sup>J(CH) in methane, 167.8 Hz<sup>16</sup> and 125.306 Hz,<sup>17</sup> respectively, is an indication that the *s* character on the C atom of the bridgehead C—H bond in the former is notably larger than that in the methane C—H bond.<sup>18</sup> A larger *s* character implies a smaller *p* character, and it is known<sup>19</sup> that a bond polarizability is larger the larger the *p* character of that bond.

The *s* and *p* characters at the C<sub>3</sub> atom in the C<sub>3</sub>—M<sub>α</sub> bond represented by the LMO  $|i\rangle$  can be estimated as the mean value over  $|i\rangle$  of the orthogonal projector  $P_\mu^\perp$  ( $\mu = s, p$ ) on the subspace spanned by the  $\mu$ -type atomic orbitals centered on C<sub>3</sub>; that is,

$$C_\mu = \langle i | P_\mu^\perp | i \rangle$$

Values thus calculated for  $M = \text{H, F, and CH}_3$  in **I** ( $X = \text{H}$ ) are compared in Table II with those calculated in CH<sub>3</sub>M. It is observed that, for a given *M*, the decrease in the *p* character follows that of the bond polarizability.

The C<sub>3</sub>—M<sub>α</sub> bond polarizability yields a measure of the C<sub>3</sub>—M<sub>α</sub> bond distortion due to a uniform electric field along the bond direction. In compounds **I** the *X* substituent can be thought to provide an electric field with this direction. The more electronegative the *X* is, the larger the positive charge at C<sub>1</sub>. The distortion of the electronic density of the C<sub>3</sub>—M<sub>α</sub> bond is taken into account in the corresponding occupied LMO obtained from the ground state wave function of the substituted compound. As described previously for  $M = \text{H}$

**TABLE II.** *s* and *p* character at C Atom of C—M ( $M = \text{H, F, C}$ ) Bonds in **I** and in CH<sub>3</sub>M ( $M = \text{H, F, CH}_3$ ) (All Values in a.u.)

	<i>M</i> = H	<i>M</i> = F	<i>M</i> = C
(a) CH <sub>3</sub> X			
C <sub>s</sub>	0.372	0.160	0.385
C <sub>p</sub>	0.544	0.245	0.392
(b) 1-X-bicyclo[1.1.1]pentane			
C <sub>s</sub>	0.541	0.229	0.517
C <sub>p</sub>	0.379	0.202	0.284

within the INDO approach,<sup>1</sup> such distortion manifests itself as an increase in the contribution of the *s*-type AO of the C<sub>1</sub> atom to the LMO describing the C<sub>3</sub>—M<sub>α</sub> bond when increasing the *X* electronegativity. It was shown in that work that this extension of the C<sub>3</sub>—H bond toward the C<sub>1</sub> atom increases the Fermi contact interaction of electrons that bond with the C<sub>1</sub> nucleus, thus yielding a larger contribution to the <sup>3</sup>J(C<sub>1</sub>H) coupling constant.

To verify if such an electrostatic effect can be considered the main one defining the large substituent effects on <sup>3</sup>J(C<sub>1</sub>H) couplings, the following theoretical approach is used. In **I**, the electrostatic effect on the C<sub>3</sub>—M<sub>α</sub> bond can be reproduced artificially by creating an electrostatic field which attracts electrons to the *X* center. This can be accomplished by taking  $X = \text{H}$  and placing an additional positive charge at the site of the proton. Of course, this procedure will distort the C<sub>1</sub>—H bond in a different way from that of an electronegative substituent, like, for instance,  $X = \text{F}$ . However, it can be considered that the electrostatic effect in the region of the C<sub>3</sub>—M<sub>α</sub> bond is similar to that of an electronegative substituent, provided an adequate value for that charge is chosen.

In Table III, the calculated Fermi contact (FC) contributions to <sup>3</sup>J(C<sub>1</sub>M<sub>α</sub>) couplings ( $M = \text{H, CH}_3$ ) in **I** ( $X = \text{H; H}^\delta, \text{F}$ ) are shown, where H<sup>δ</sup> stands for an H atom such that, at the site of its nucleus, a + $\delta$  charge is placed (noncontact contributions are assumed to be by far much smaller than the FC one). Experimental values are quoted in parentheses. The cage geometry employed to carry out the  $X = \text{H}^\delta$  calculation is that obtained when optimizing the geometry for the  $X = \text{F}$  compound. It is found that for  $\delta = +0.25$  a.u. the calculated <sup>3</sup>J(C<sub>1</sub>M<sub>α</sub>) couplings are similar to both the calculated and the measured ones<sup>1</sup> in **I** with  $X = \text{F}$ . As mentioned previously, effects other than the elec-

**TABLE III.**  
Fermi Contact Contribution to  ${}^3J(\text{C}_1\text{M}_\alpha)$  Couplings  
( $\text{M} = \text{H}, \text{CH}_3$ ) in **I** ( $\text{X} = \text{H}, \text{F}, \text{H}^\delta$ ).

X	${}^3J(\text{C}_1\text{H})$	${}^3J(\text{C}_1\text{C})$
H	11.74 (10.0)	11.38 (9.7)
F(opt.) <sup>b</sup>	24.67 (27.4)	17.93
H <sup>δa</sup>	28.82	19.22
F(unopt.) <sup>b</sup>	31.08	19.73

Experimental values are indicated in brackets below the corresponding calculated ones. All couplings in hertz.

<sup>a</sup>H<sup>δ</sup> stands for the H atom such that at the site of its nucleus a  $\delta = +0.25$  a.u. charge is placed.

<sup>b</sup>opt.: calculation carried out with the  $\text{X} = \text{F}$  optimized geometry; unopt.: calculation carried out with the optimized geometry of the parent compound ( $\text{X} = \text{H}$ ) taking the standard value for the F—C bond length.

trostatic one are also defining the notorious substituent effects observed on  ${}^3J(\text{C}_1\text{M}_\alpha)$  couplings. They were discussed in some detail in ref. 1. Here, the effect of the cage geometry is also studied using a different approach, namely, using two different cage geometries to carry out calculations in **I** ( $\text{X} = \text{F}$ ,  $\text{M} = \text{H}, \text{CH}_3$ ). These are: (a) the respective fully optimized geometries; and (b) the optimized geometry of the respective parent compound **I** ( $\text{X} = \text{H}$ ,  $\text{M} = \text{H}, \text{CH}_3$ ). Calculations carried out with the (a) geometries yield  ${}^3J(\text{C}_1\text{M}_\alpha)$  couplings somewhat smaller than those obtained with the (b) geometries. The geometry changes can easily be rationalized with Bent's rule. In fact, upon substitution by a more electronegative substituent, like, for instance,  $\text{X} = \text{F}$ , the  $\text{C}_1$   $s$ -character of the  $\text{C}_1$ —C cage bonds increases. Such change is consistent with a decrease of the  $\text{X}$ — $\text{C}_1$ —C angle as it is in fact obtained in the optimized geometry, where the bridgehead  $\text{C}_1 \cdots \text{C}_3$  distance is ca. 0.077 a.u. shorter than in the parent compounds. It is interesting to observe that the geometry effect on the  ${}^3J(\text{C}_1\text{M}_\alpha)$  coupling is noticeably larger for  $\text{M} = \text{H}$  than for  $\text{M} = \text{CH}_3$ .

As part of this work, a few members of series **I** were synthesized and their respective  ${}^3J(\text{C}_1\text{M}_\alpha)$  coupling constants measured. The corresponding experimental details will be given in a forthcoming study.<sup>20</sup> The measured couplings are collected in Table IV where the corresponding substituent effects,  $E_{(\text{X})}$ , are also shown. Values for **I** with  $\text{X} = \text{H}$ ,  $\text{OCH}_3$ , and  $\text{Cl}$  taken from ref. 1 are also displayed in Table IV. It is worthy of noting that, for  $\text{M} = \text{H}$ ,  $\text{F}$ , and  $\text{CH}_3$ , the respective  $E_{(\text{X})}$  sub-

**TABLE IV.**  
Experimental  ${}^3J(\text{C}_1\text{M})$  NMR Spin-Spin Coupling  
Constants in **I**,  $\text{M} = \text{H}, \text{F}, \text{CH}_3$  and  $\text{Sn}(\text{CH}_3)_3$  and  
 $\text{X} = \text{H}, \text{Cl}$ , or  $\text{OCH}_3$ .

X	M	${}^3J(\text{C}_1\text{M})$	$E_{(\text{X})}$
H	H	10.0 <sup>a</sup>	
OCH <sub>3</sub>	H	20.8 <sup>a</sup>	2.08
Cl	H	31.5	3.15
H	F	42.4	
Cl	F	108.0	2.55
H	CH <sub>3</sub>	9.7	
Cl	CH <sub>3</sub>	18.6	1.92
H	Sn(CH <sub>3</sub> ) <sub>3</sub>	134.9	
OCH <sub>3</sub>	Sn(CH <sub>3</sub> ) <sub>3</sub>	201.0	1.49

The respective substituent effects,  $E_{(\text{X})}$ , are also shown. All couplings in hertz.

<sup>a</sup>This work.

stituent effects follow the same trend as the C—H, C—F, and C—C bond polarizabilities in **I** ( $\text{X} = \text{H}$ ) shown in Table I. The C—Sn bond polarizability could not be calculated because heavy-atom-containing molecules cannot be studied with the SYSMO program. However, from values displayed in Table IV, it can be expected that the C—Sn bond polarizability in **I** [ $\text{M} = \text{Sn}(\text{CH}_3)_3$ ] is somewhere between those of the C—F and C—C bonds in **I** ( $\text{X} = \text{H}$ ,  $\text{M} = \text{F}$ ) and in **I** ( $\text{X} = \text{H}$ ,  $\text{M} = \text{CH}_3$ ) respectively. However, it should be closer to that of the former than to that of the latter. This implies that the C—Sn bond polarizability is larger than that of the C—C bond. This result is in agreement with assumptions commonly made about the polarizability of a C—Y bond where Y is a Group IV element,<sup>21</sup> namely, that it increases when going down the Periodic Table.

## Conclusions

Studies on the interactions transmitted through the bridgehead carbon atoms in compounds of type **I** presented in this work strongly support the rationalization made previously<sup>1</sup> on the surprisingly large substituent effects on  ${}^3J(\text{C}_1\text{M}_\alpha)$  spin-spin coupling constants in series **I** with  $\text{M} = \text{H}$ .

The  $\text{C}_3$ — $\text{M}_\alpha$  ( $\text{M}_\alpha = \text{H}, \text{F}, \text{C}$ ) bond polarizabilities calculated in **I** ( $\text{X} = \text{H}$ ;  $\text{M} = \text{H}, \text{F}, \text{CH}_3$ ) follow a trend similar to that of the  $E_{(\text{X})}$  substituent effects on  ${}^3J(\text{C}_1\text{M}_\alpha)$  coupling constants measured in this work in **I** compounds ( $\text{X} = \text{Cl}$ ;  $\text{M} = \text{H}, \text{F}$ ,

CH<sub>3</sub>). These bond polarizabilities are conspicuously different from those calculated in unstrained compounds. This indicates that the C<sub>3</sub>—M<sub>α</sub> bond polarizabilities depend strongly on the hybridization at the bridgehead C atom. This dependence is such that the polarizability decreases when increasing the C<sub>3</sub> *s* character of the C<sub>3</sub>—M<sub>α</sub> bond.

Looking for experimental evidence supporting this conclusion, it is of interest to compare the <sup>3</sup>*J*(C<sub>1</sub>H) and <sup>3</sup>*J*(C<sub>1</sub>C<sub>Me</sub>) couplings in **I** (*X* = H; *M* = H, CH<sub>3</sub>) with the analogous couplings in bicyclo[2.1.1]hexanes, **II**, (*X* = H, *M* = H and CH<sub>3</sub>); that is, the respective <sup>3,4</sup>*J*(C<sub>1</sub>H) and <sup>3,4</sup>*J*(C<sub>1</sub>C<sub>Me</sub>) couplings. This comparison is displayed in Table V, where the experimental bridgehead C⋯C distances in the parent compounds are also compared. Both types of couplings show opposite trends—that of the *J*(C<sub>1</sub>C<sub>Me</sub>) couplings is in agreement with what it could be expected.<sup>25</sup> In fact, in **I** the following points should be recalled: (a) the bridgehead C<sub>1</sub>—H and C<sub>3</sub>—C<sub>Me</sub> bonds are collinear, and this does not hold in **II**; and (b) the bridgehead C⋯C distance is smaller in the former than in the latter. These two facts would render larger analogous couplings in **I** than in **II**. However, this is not the trend depicted by the *J*(C<sub>1</sub>H) couplings, and there should be a further effect on them. This further effect seems to provide experimental support for the results presented in this article. In fact, it is known that the C<sub>4</sub> *s* character of the C<sub>4</sub>—H bond in **II** (*M* = H) is smaller than the C<sub>3</sub> *s* character of the C<sub>3</sub>—H bond in **I** (*M* = H).<sup>26</sup> Therefore, the bond polarizability effect on the <sup>3,4</sup>*J*(C<sub>1</sub>H) coupling in **II** (*M* = H) should be larger than that in <sup>3</sup>*J*(C<sub>1</sub>H) in **I**, compensating the two effects (a) and (b), quoted previously. According to the values shown in Table I, the hybridization effect on a C—C bond polarizability is notably lower than in a C—H bond. For this reason

the bond polarizability effect cannot overcome the (a) and (b) effects on <sup>3,4</sup>*J*(C<sub>1</sub>C<sub>Me</sub>) and <sup>3</sup>*J*(C<sub>1</sub>C<sub>Me</sub>) couplings displayed in Table V.

Another interesting example is the experimental value of <sup>4</sup>*J*(CF) couplings in 4-substituted fluorocubanes, **III**,<sup>27</sup> where <sup>3</sup>*J*(CF) = 13.54 Hz in the parent compound and <sup>4</sup>*J*(CF) = 23.47 Hz in 4-Cl fluorocubane were measured. These values yield a substituent effect *E*<sub>(Cl)</sub> = 1.73, which, although it is smaller than the *E*<sub>(Cl)</sub> value in **I** (displayed in Table IV), it is a very large value taking into account that the bridgehead C⋯C distance in the parent compound of **III** is 2.7 Å, which is notably larger than the bridgehead C⋯C distance in the parent compound of **I**, 1.844 Å.<sup>23</sup>

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**TABLE V.**  
Comparison of <sup>3</sup>*J*(C<sub>1</sub>H) and <sup>3</sup>*J*(C<sub>1</sub>C<sub>Me</sub>) Couplings in **I** with <sup>3,4</sup>*J*(C<sub>1</sub>H) and <sup>3,4</sup>*J*(C<sub>1</sub>C<sub>Me</sub>) Couplings in **II** (*X* = H, *M* = H, CH<sub>3</sub>).<sup>a</sup>

	<i>M</i>	<b>I</b>	<b>II</b>
<i>J</i> (C <sub>1</sub> H) (Hz)	H	10.0 <sup>b</sup>	12.6 <sup>c</sup>
<i>J</i> (C <sub>1</sub> C) (Hz)	CH <sub>3</sub>	9.7 <sup>d</sup>	7.5 <sup>c</sup>
<i>D</i> (Å)		1.844 <sup>e</sup>	2.172 <sup>f</sup>

<sup>a</sup>The experimental bridgehead C⋯C distances, *D*, in the parent compounds are also displayed. <sup>b</sup>Taken from ref. 1.

<sup>c</sup>Taken from ref. 2. <sup>d</sup>This work. <sup>e</sup>Taken from ref. 23. <sup>f</sup>Taken from ref. 24.

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